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Newport
South Wales
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I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

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Signed

Dated 21 October 2003

Patents Form 1/77

Patents Act 1977
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THE PATENT OFFICE
08 OCT 2002

The Patent Office

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P01/7700 0.00-0223350.0

1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP9 1RH

1. Your reference — RSJ07615GB

2. Patent application number *(The Patent Office will fill in this part)* — 0223350.0

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

City Technology Limited
City Technology Centre
Walton Road
Portsmouth, PO6 1SZ
GREAT BRITAIN

Patents ADP number *(if you know it)* 6217830001

If the applicant is a corporate body, give the country/state of its incorporation — Great Britain

4. Title of the invention — FLUE GAS SENSORS

5. Name of your agent *(if you have one)* — Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Broadgate House
7 Eldon Street
London
EC2M 7LH

Patents ADP number *(if you know it)* — 745002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	6
Claim(s)	CF
Abstract	
Drawing(s)	7+7

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	NO

11. For the applicant
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 08/10/02

12. Name and daytime telephone number of person to contact in the United Kingdom

SKONE JAMES, Robert Edmund
020 7377 1377

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

f) *For details of the fee and ways to pay please contact the Patent Office.*

FLUE GAS SENSORS

Concern over the generation of dangerous levels of CO by malfunctioning or incorrectly adjusted domestic gas appliances has been rising in recent years. To comply with current ANSI standards in the US and ever increasing constraints on CO_2 emissions in the EU, there is an increasing interest in combustion or flue monitoring technology.

Flue gas atmospheres represent particularly aggressive conditions. Temperatures range from 50°C to 200°C (depending on the degree of cooling by the heat exchanger and whether or not the furnace is of a non-condensing or condensing design) while the gas itself is saturated with water vapour and creates reducing conditions due to low overall oxygen levels, typically ~ 5%. Other components are CO_2 and CO, typically at around 8% and 30ppm respectively, with the balance being predominantly nitrogen. In the event of the flue being restricted, or of the air/fuel pre-mix not being correct, the O_2 level in the flue decreases. The CO level remains unchanged until the system becomes fuel-rich, whereupon it increases rapidly. Figure 1 shows typical combustion behaviour for a pre-mixed boiler where such changes in O_2 and CO levels are clearly highlighted.

There are less commonly encountered situations in which significant changes in CO or O_2 level may occur without a major change in the concentration of the other species. Furthermore, "overgassing" may occur in which case fuel species or other partial combustion products such as H_2, CH_4 and heavier hydrocarbons can appear in the flue. A simple, reliable means of rapidly detecting either a fall in O_2 content and/or a rise in CO level is therefore required, and if such means additionally allows the detection of these other undesirable circumstances, this will confer further advantage. Although the primary application addressed here is that of a safety alarm

activated in the event of malfunction, it will also be clear that one or more of these conditions may also be used to act as a control parameter to ensure safe and efficient operation of the combustion plant.

Metal oxide semiconductor sensors typically operate at elevated temperatures somewhat higher than those encountered in small flues. Because of the demanding operating conditions, and their ability to respond to a number of parameters indicating potentially dangerous situations, they represent a much more appropriate means of monitoring CO in this environment than other comparatively low cost sensors. For example, liquid electrolyte fuel cells are widely used in the industrial environment to detect dangerous levels of CO, but they are incapable of surviving for any extended period in the atmospheric conditions of the flue due to their reliance on aqueous electrolytes. Furthermore, they generally only respond significantly to a single chemical species, so separate sensors would be required to measure CO and O_2. Catalytic sensors, on the other hand, lack sensitivity to CO at the toxic levels of interest, are prone to poisoning of their catalysts and may give ambiguous or unreliable readings under changing oxygen levels.

Since the flue gas application is a safety critical one, where the lives of numerous persons adjacent to a malfunctioning boiler may be put in jeopardy, sensing technologies which offer fail safe operation are naturally preferred. The hot humid conditions within the flue, combined with the reducing nature of the flue gas and the potential occurrence of poisons requires that the chosen technique should be robust against corrosion and breakage of sensor connections, or loss in sensitivity due to surface poisoning. Some semiconductor materials which are widely and successfully used in other gas sensing applications are ill suited to this demanding role. The most commonly employed types are based on n-type tin oxide additionally containing precious metal catalyst additives

(for example those manufactured by Figaro and other companies), but these materials fail to meet the requirements of the application for a number of reasons;

(a) Although they can respond rapidly to changing oxygen levels as required, such responses may be wholly or partially irreversible due to bulk reduction of the oxide lattice: Such effects can occur even at comparatively moderate operating temperatures.

(b) They have a limited ability to function in the presence of species which can poison the surface sites governing the gas response. Moreover, such poisoning is not necessarily detectable other than by challenging the device with a calibration gas mixture, which is an impractical requirement in a domestic situation.

(c) The increased resistance which they provide on contact failure is in opposition to the reduced resistance output which occurs on detection of increased levels of CO or reduced oxygen content. As such, it is not immediately recognised by a simple signal processing system as indicative of a dangerous condition.

(d) They are particularly prone to interference from the effects of water vapour, which can swamp the signals derived from the species of interest.

In all these respects, the n-type tin oxide device does not fail safe and as such is unsuitable for the intended application.

Although much less widely used than n-type systems, p-type semiconductor materials are known in gas sensing applications (see, for example, Chapter 4 in "Sensor Materials" by P.T. Moseley & A.J. Crocker, IoP Publishing 1996). However, their specific advantages in the demanding flue gas application have not previously been realised, appreciated or quantified.

We have found that p-type mixed metal oxide semiconducting sensors of the first, second and third order transition metal series are particularly well suited for flue gas detection, for the following reasons;

(i) They exhibit excellent chemical stability in wet reducing atmospheres, due to the particularly high formation energies of the oxides.

(ii) They are resilient to the effects of typical poisons such as mercaptans and silicone sealants since they do not rely upon the presence of precious metal catalysts to generate the gas sensitive signal.

(iii) They undergo a rapid and reversible increase in resistance in response to a decrease in oxygen and/or an increase in CO content of the surrounding atmosphere. The relationship between the electrical resistance of such sensors, which is the response parameter used, and the carbon monoxide and oxygen concentrations in the test atmosphere follows a relationship of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

[CO] is the carbon monoxide concentration

A, B are constants which depend on the sensor resistance under reference conditions

x is a parameter which depends on the point defect chemistry of the oxide system.

There may be slight departures from this relationship in dry conditions and at low carbon monoxide concentrations (< 100ppm CO).

(iv They also possess a significant reversible response to other reducing species of interest.

(v) Connection faults giving rise to an apparent resistance rise can be identified as a dangerous state by a simple alarm system a since the target gases will also produce a resistance increase.

Although a wide range of p-type materials are in principle suitable for such applications, the following examples are based on tests performed using a standard commercial devices marketed for CO monitoring (Capteur sensor CAP07, City Technology Ltd). This design employs p-type oxides of the Cr-Ti-O system, for example as described in patent applications PCT/GB01/02046, EP0940673A2 and EP0656111B1.

As is evident from the above relationship, the sensor resistance increases with both increasing CO concentration (Figure 2) and decreasing O_2 concentration (Figure 3). Thus, whenever the air supply drops or when there is incomplete combustion for other reasons, the sensor will detect the condition as a result of this combined effect. Figure 4 demonstrates this for a range of sensors exposed to various CO/O_2 combinations. It can be seen that the sensor resistance in 200ppm CO at 10%O_2 is comparable to that in 100ppm CO at 5% O_2 which in turn is comparable to that at <50ppm at 2.5% O_2. The sensors in this example were carefully selected from a standard batch, representing the two extremes in performance, i.e. at both ends of the 95% confidence range.

In addition to the sensor being alert to the presence of CO and varying O_2 concentrations, it will also respond to the presence of other relevant gases, such as H_2, CH_4, and other heavier hydrocarbon fuels. Figure 5 shows typical responses to these gases over a range of different concentrations. The error bars represent the full range of responses for 10 sensors. A continuous atmosphere of 5% O_2 was maintained in this test to replicate conditions in the boiler flue.

If the sensor is to be considered for use in boiler flue applications, it is important that its performance should not degrade while continuously operated over a time period commensurate with the life of the boiler or an acceptable maintenance interval. Longevity data is not as yet available for sensors operated within the flue.

However, the performance of similar devices operated under typical domestic conditions (for which application the sensor was originally designed) meets the 1 year test requirements of the UL2034 standard for domestic fire detection applications.

Figures 6 and 7 show the performance of 3 p-type sensors in the flue of a condensing gas furnace. The sensors are based on sensing layers employing the Cr-Ti-O system and were set up to a resistance of 50 kohms in clean air at 50% relative humidity. At this resistance, the sensors are running at about 480-500°C. The sensors were installed in a vertical tube ducting the flue gases away from the heat exchange coils. The temperature of the flue gases at this point was 40°C. As a cross-check, an sample of the flue gas was extracted and cooled and then drawn across an electrochemical CO sensor (3F/F, City Technology Ltd) and an electrochemical O_2 sensor (2FO, City Technology Ltd). To create an unsafe condition, the vertical tube was restricted in stages by means of a sliding plate. It can be seen from Figures 6 and 7 that the p-type sensors respond to both a reduction in oxygen level and an increase in CO level. The combined effects of these two responses gives rise to a very large signal from the p-type sensors which could readily be used in conjunction with a variety of simple signal processing means to alert users of these potentially dangerous conditions.

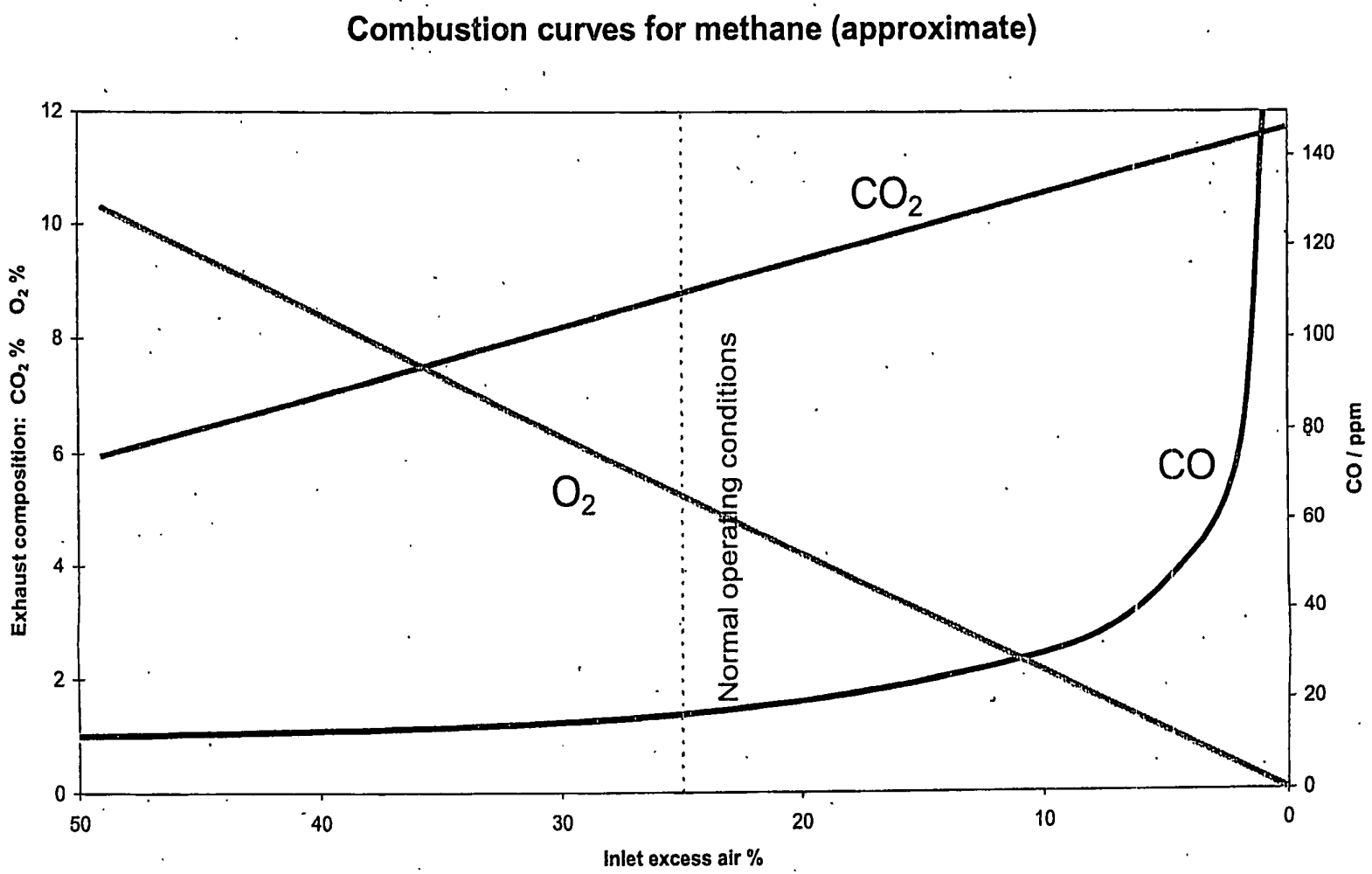

Figure 1 : Typical combustion curves for a pre-mixed boiler

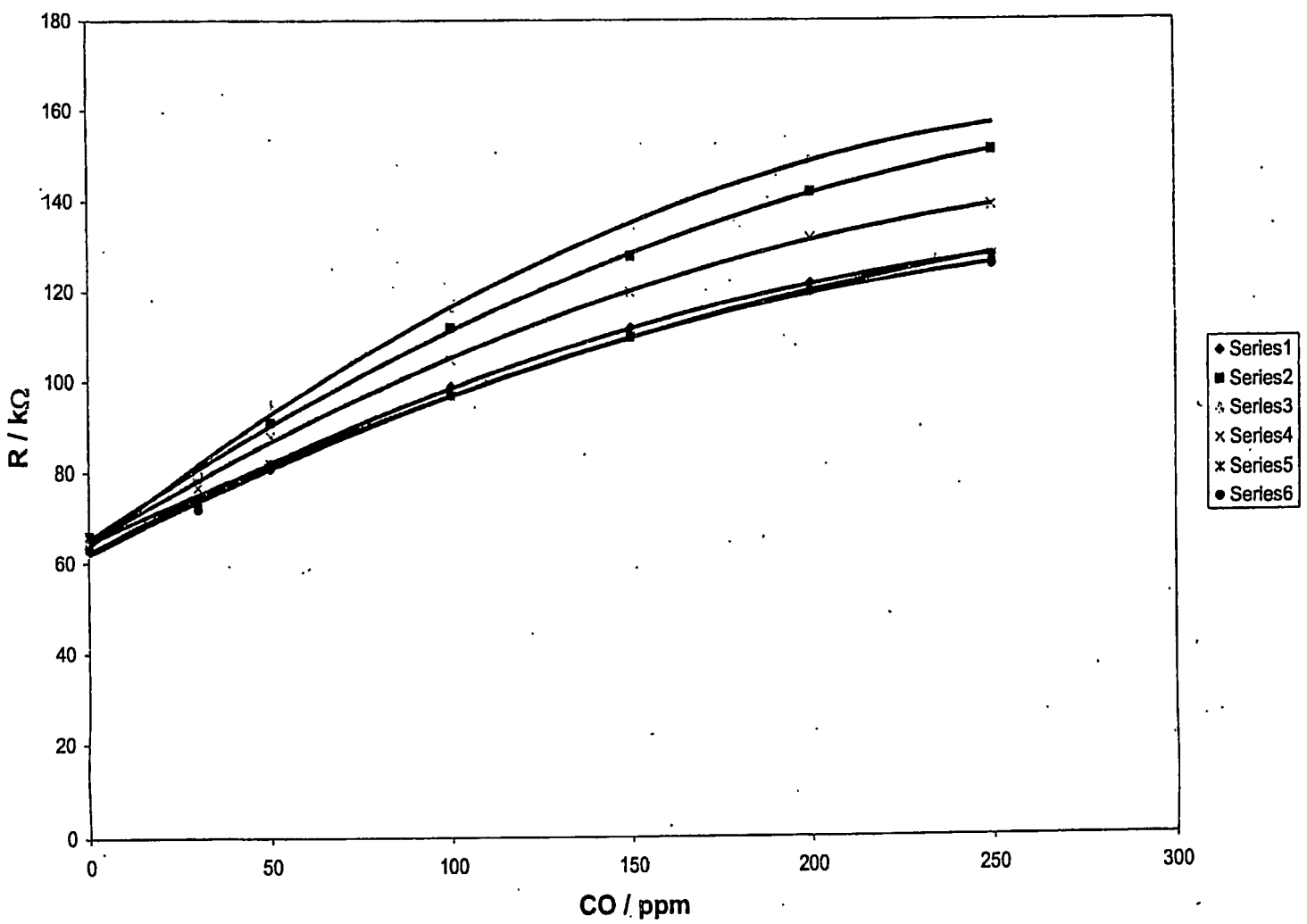

Figure 2 : Variation in sensor resistance with CO concentration

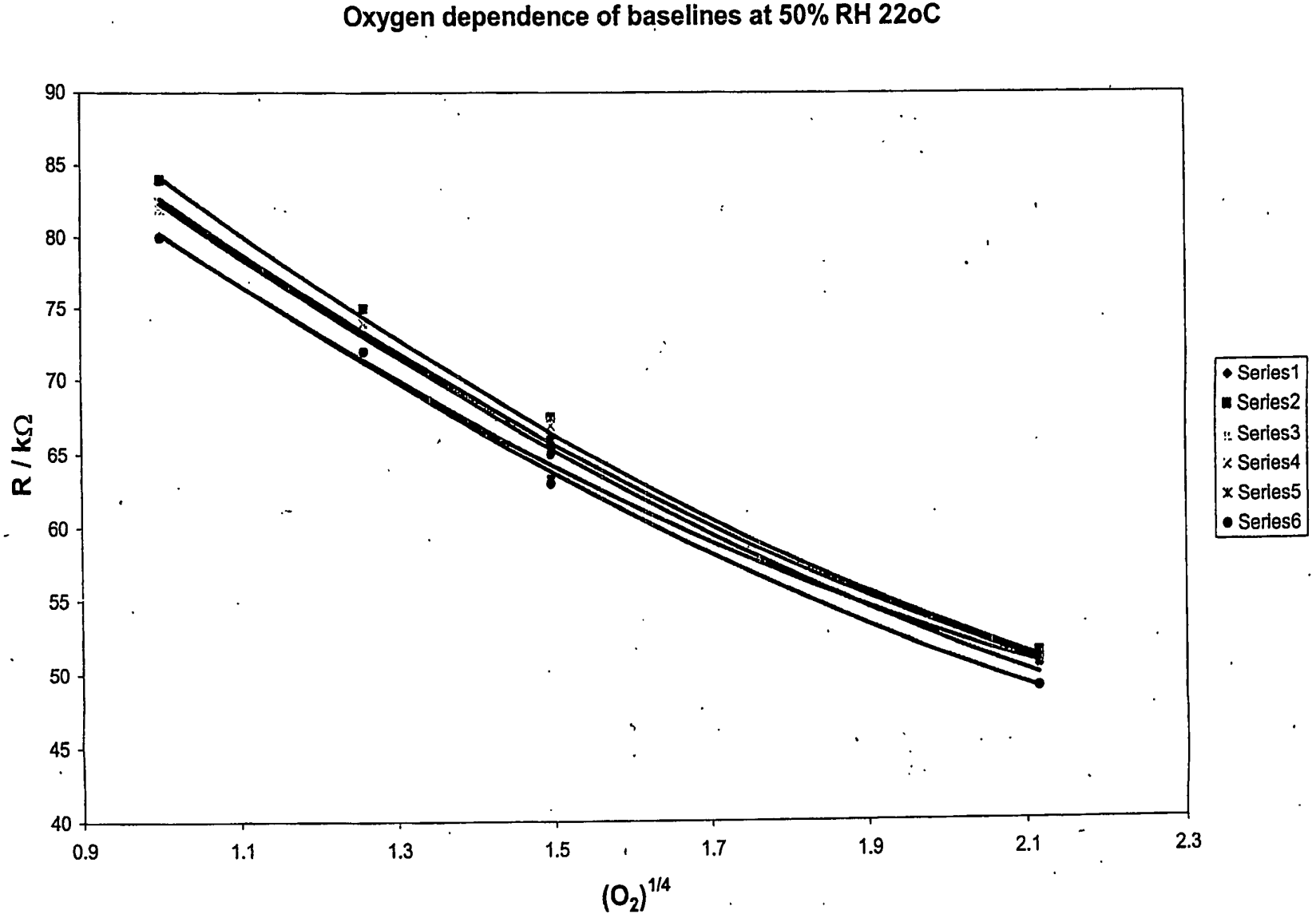

Figure 3 : shows the variation in sensor resistance with varying O_2 concentration

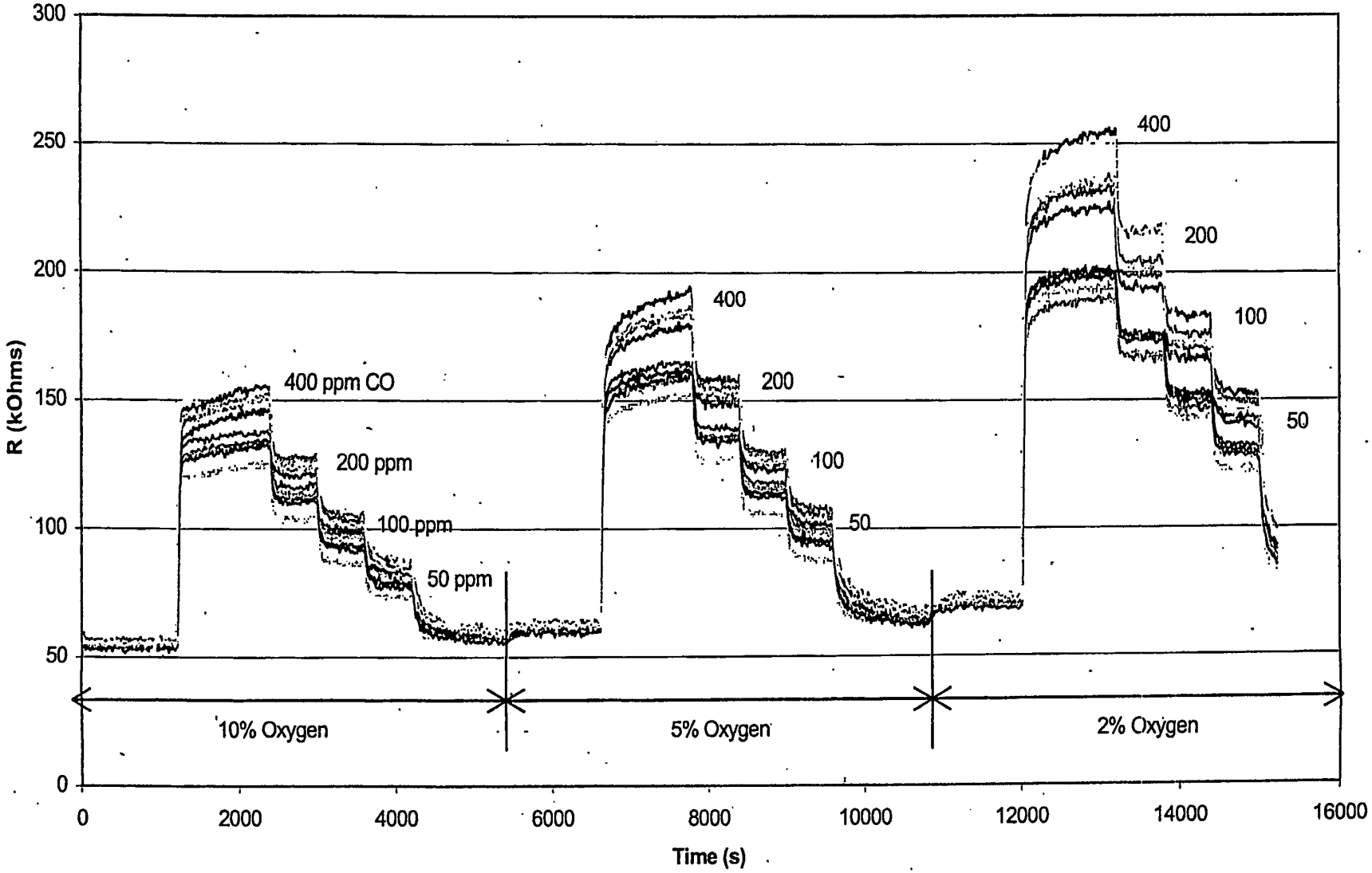

Figure 4 : Dependency of sensor resistance on CO and O_2 concentrations

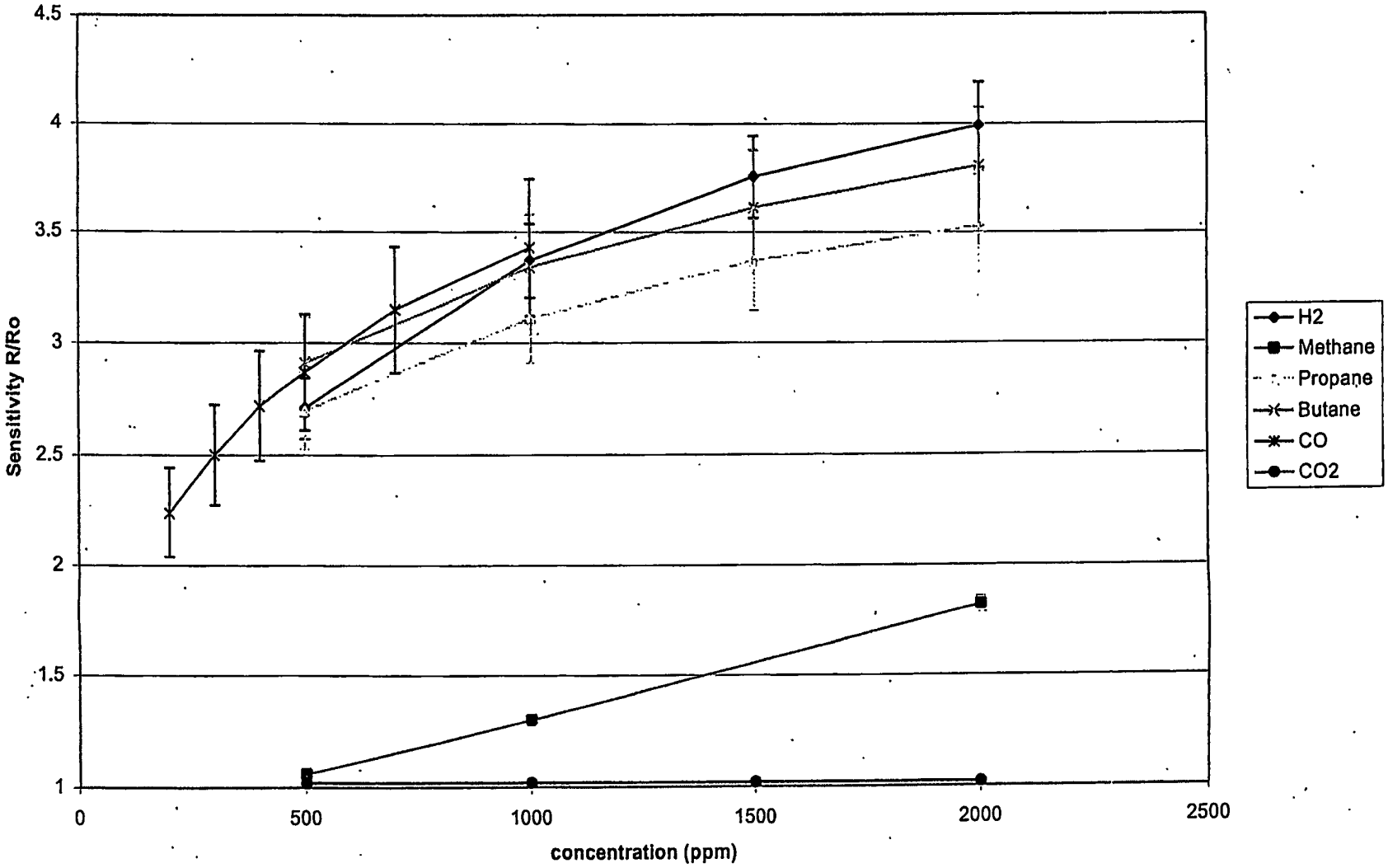

Figure 5 : Response of CO sensor to other gases in 5%O_2 and 24% relative humidity.

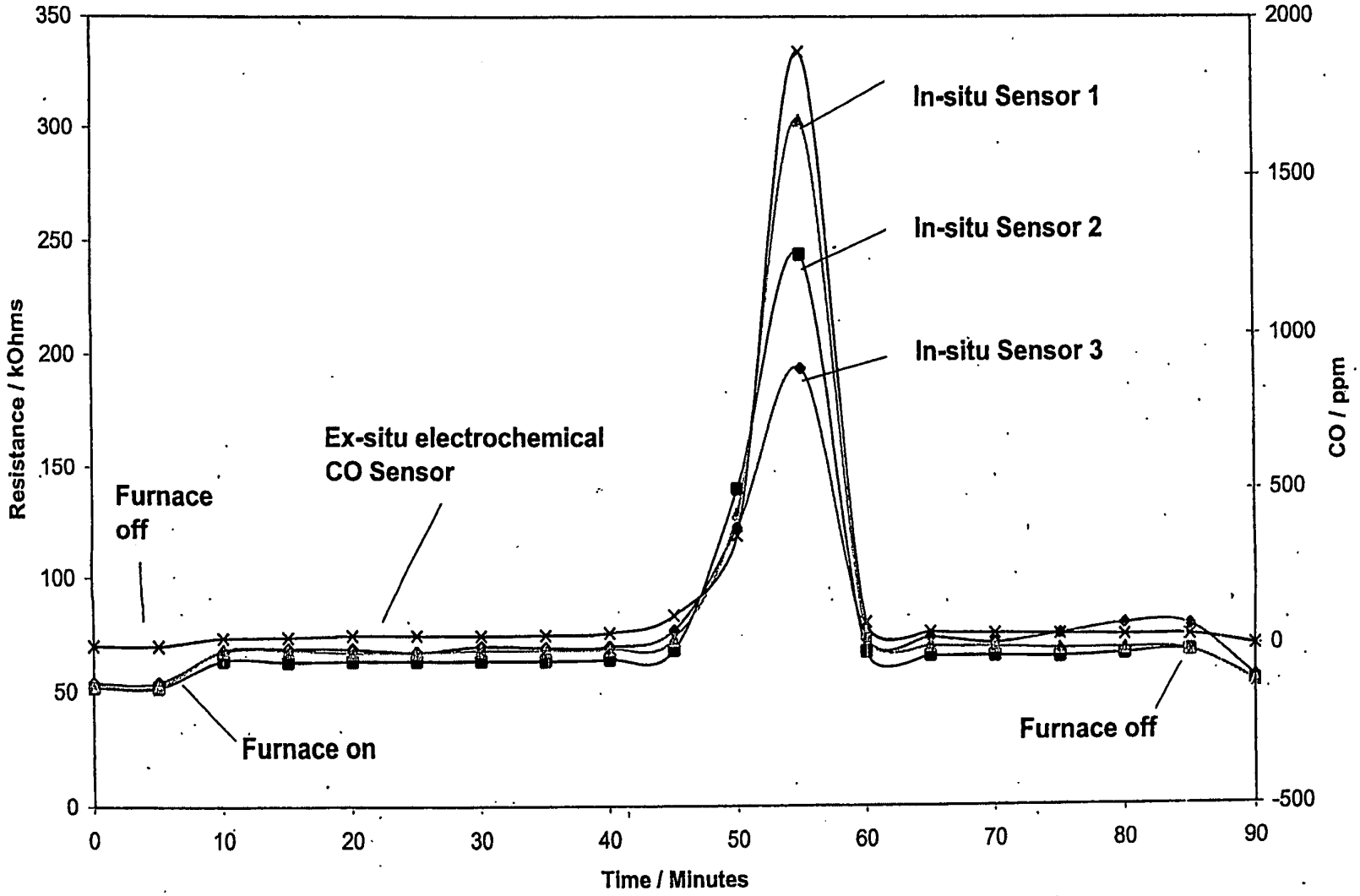

Figure 6: Behaviour of 3 p-type MMOS sensors in a flue atmosphere. The response of an electrochemical CO sensor in a cooled extracted sample of the gas is also shown.

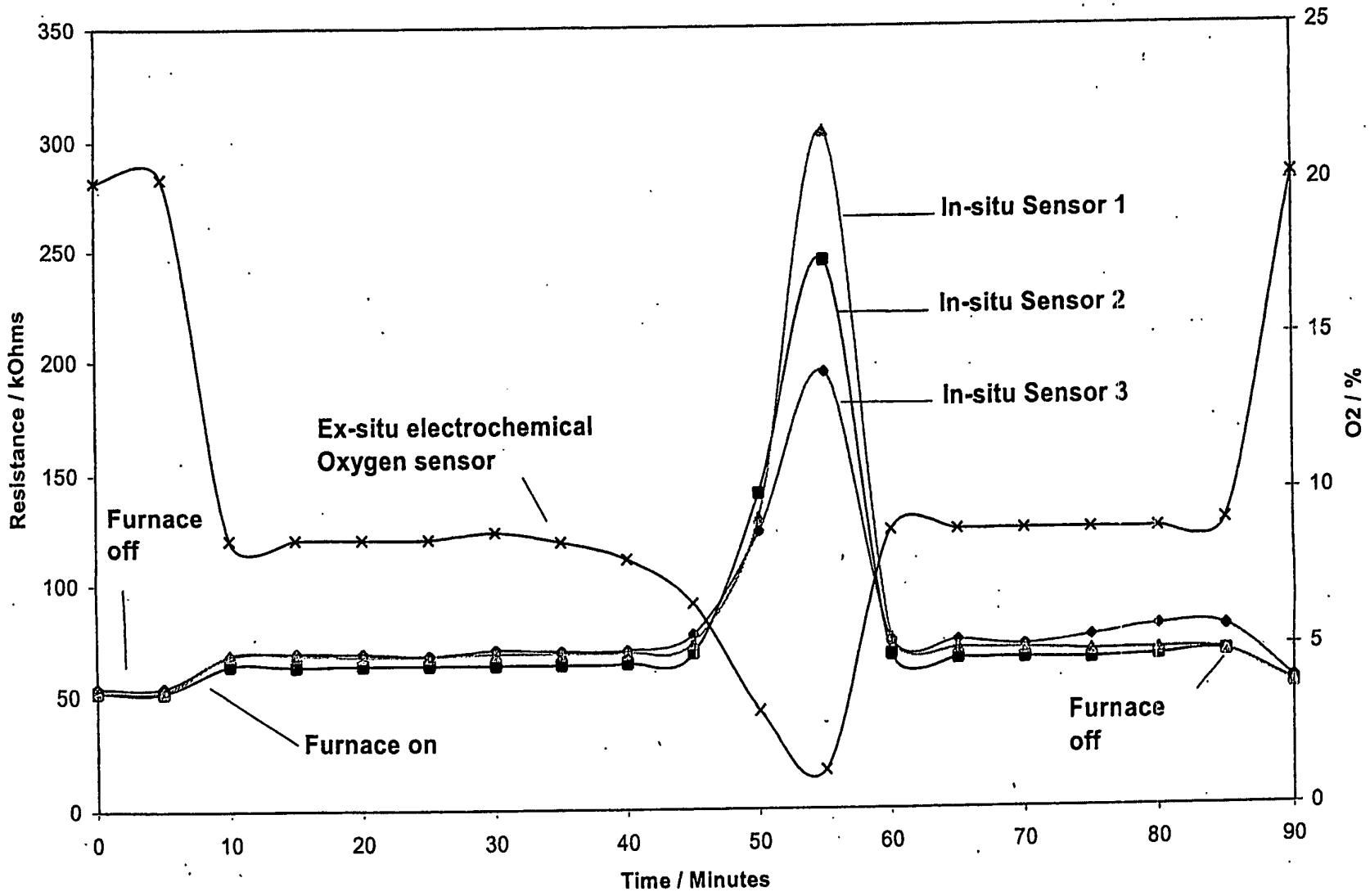

Figure 7: Behaviour of 3 p-type MMOS sensors in a flue atmosphere. The response of an electrochemical O_2 sensor in a cooled extracted sample of the gas is also shown.